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(54) Internal Hydroxy Mixed Ethers

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Internal hydroxy mixed ethers

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to internal hydroxy mixed ethers obtained by ring opening of epoxides of unsaturated fatty acid esters with fatty alcohol polyglycol ethers, to a process for their production and to their use as an auxiliary in the dewatering of solids.

2. STATEMENT OF RELATED ART

There are many branches of industry, for example mining or sewage treatment, where large quantities of fine-particle solids of high water content accumulate and have to be dewatered before subsequent processing or disposal as waste. For example, the dewatering of hard coal or coke is a key process in the cleaning of coal-based fuels. The upper limits to the water content of these materials as required by the market are often difficult to adhere to, for example because mine-run coal accumulates in very fine-particle form due to the extensive mechanization of underground coal mining. At the present time, around 38% of the gross output consists of fine coal with a particle diameter in the range from 0.5 to 10 mm. Another 14% consists of ultrafine coal with even smaller particle diameters.

It is known that certain surfactants are suitable as auxiliaries for the dewatering of water-containing fine-particle solids suspensions, particularly iron ore concentrates or hard coals, by which their residual moisture content can be reduced. For example, dialkyl sulfosuccinates (US 2,266,954) and nonionic surfactants of the fatty alcohol polyglycol ether type (Erzmetall 30, 292 (1977)) have been described as surface-active dewatering aids of the type mentioned above. However, these surfactants are attended by the disadvantage of high foaming which leads to serious problems, particularly during the recirculation of water typical of cleaning plants.

DE-A1-39 18 274 (Henkel) describes alkyl-end-capped ß-hydroxyalkyl ethers, so-called hydroxy mixed ethers, which are produced by ring opening of α-olefin epoxides with fatty alcohol ethoxylates and which are used as low-foaming auxiliaries in the dewatering of solids suspensions. Although good results are obtained with these auxiliaries in the dewatering of solids, they are attended by the disadvantage of unsatisfactory low-temperature behavior. Crystals can form at temperatures of only 10 to 15°C, particularly where the suspensions are stored outdoors, which adversely affects the pumping and flow behavior of the products and hence seriously impairs their intended use.

Accordingly, the problem addressed by the present invention was to provide new hydroxy mixed ethers which would show improved low-temperature behavior for otherwise the same performance properties.

DESCRIPTION OF THE INVENTION

The present invention relates to internal hydroxy mixed ethers which are obtained by subjecting epoxides of unsaturated fatty acid esters with fatty alcohol polyglycol ethers corresponding to formula (I):

$$R^1O-(CH_2\overset{\overset{\displaystyle R^2}{|}}{C}HO)_nH \qquad (I)$$

in which R^1 is a linear or branched, aliphatic C_{4-22} hydrocarbon radical and R^2 is hydrogen or a methyl group, to ring opening.

It has surprisingly been found that the internal hydroxy mixed ethers according to the invention show distinctly better low-temperature behavior than the known terminal hydroxy mixed ethers according to DE-A-39 18 274, more particularly lower pour points, for equally good and, in some cases, slightly improved performance properties.

The present invention also relates to a process for the production of internal hydroxy mixed ethers, in which epoxides of unsaturated fatty acid esters with fatty alcohol polyglycol ethers corresponding to formula (I):

$$R^1O-(CH_2\overset{\overset{\displaystyle R^2}{|}}{C}HO)_nH \qquad (I)$$

in which R^1 is a linear or branched, aliphatic C_{4-22} hydrocarbon radical and R^2 is hydrogen or a methyl group, are subjected to ring opening.

In the context of the invention, epoxides of unsaturated fatty acid esters are, for example, addition products of oxygen with the double bonds of mono- or polyunsaturated fatty acid lower alkyl esters corresponding to formula (II):

$$R^3CO\text{-}OR^4 \qquad \text{(II)}$$

in which R^3CO is an unsaturated acyl radical containing 16 to 22 carbon atoms and R^4 is a linear or branched alkyl radical containing 1 to 4 carbon atoms. Typical examples are epoxidized methyl, ethyl, propyl or butyl esters of palmitoleic acid, oleic acid, elaidic acid, petroselic acid, linoleic acid, linolenic acid, gadoleic acid and erucic acid and technical mixtures thereof. The epoxides used may be present in completely epoxidized form, although they may even contain double bonds. The degree of epoxidation, based on the double bonds available, is 50 to 100% and, more particularly, 70 to 95%. Since technical cuts of unsaturated fatty acid lower alkyl esters still containing saturated components are normally used to produce the epoxidized fatty acid esters, the starting epoxides may therefore also contain small amounts of saturated fatty acid lower alkyl esters. The preferred starting material is oleic acid methyl ester epoxide having an epoxide oxygen content of 4.5 to 5.1% by weight.

In addition to the epoxides of unsaturated fatty acid lower alkyl esters, epoxidized unsaturated fatty acid glycerol esters corresponding to formula (III):

$$\begin{array}{l} CH_2O\text{-}COR^4 \\ | \\ CH\text{-}O\text{-}COR^5 \\ | \\ CH_2O\text{-}COR^6 \end{array} \qquad \text{(III)}$$

in which R^4CO, R^5CO and R^6CO independently of one another represent unsaturated acyl radicals containing 16 to 24 carbon atoms, may also be used as starting materials.

Typical examples are epoxides of unsaturated triglycerides of vegetable or animal origin, for example soybean oil, rapeseed oil, olive oil, sunflower oil, cottonseed oil, peanut oil, linseed oil, beef tallow or fish oil. These starting materials may also contain saturated components. However, epoxides of fatty acid glycerol esters having an iodine value of 50 to 150 and preferably 85 to 115 are normally used. As mentioned above, both completely

and partly epoxidized esters may be used as starting materials. The preferred starting material is epoxidized soybean oil having an epoxide oxygen content of 4.5 to 6.5% by weight.

Fatty alcohol polyglycol ethers corresponding to formula (I) are suitable as the nucleophile for the ring opening of the starting epoxides mentioned. Typical examples are adducts of 1 to 30 and preferably 2 to 10 mol ethylene and/or propylene oxide with butanol, pentanol, caproic alcohol, caprylic alcohol, capric alcohol, lauryl alcohol, myristyl alcohol, isotridecyl alcohol, cetyl alcohol, palmitoleyl alcohol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, elaidyl alcohol, petroselinyl alcohol, linolyl alcohol, linolenyl alcohol, arachyl alcohol, gadoleyl alcohol, behenyl alcohol and erucyl alcohol and technical mixtures there-of such as are formed, for example, in the hydrogenation of fatty acid methyl ester fractions or aldehydes from Roelen's oxo synthesis. Adducts of 2 to 8 mol ethylene oxide with butanol and technical $C_{12/14}$ or $C_{12/18}$ coconut oil fatty alcohol cuts are preferably used.

The epoxides and the fatty alcohol polyglycol ethers may normally be used in a molar ratio of 1:0.5 to 1:1.5 and preferably in a molar ratio of 1:0.9 to 1:1.1, based on the epoxide content.

In order to ensure a short reaction time, it is advisable to carry out the ring opening reaction in the presence of basic catalysts, such as sodium methylate for example, which may be used in quantities of 0.1 to 5% by weight, based on the epoxide. Similarly, it is of advantage to carry out the ring opening reaction at temperatures in the range from 80 to 150°C and preferably at temperatures in the range from 100 to 130°C.

Industrial Applications

The internal hydroxy mixed ethers to be used in accordance with the invention support the dewatering of solids suspensions, are readily biodegradable and are distinguished by low pour points.

Accordingly, the present invention also relates to their use as auxiliaries in the dewatering of fine-particle solids suspensions, such as for example iron ore concentrates, quartz sand, hard coal or coke. Another important application is the use of the internal hydroxy mixed ethers to be used in accordance with the invention as auxiliaries in the dewatering of the solids suspensions which accumulate in the recycling of wastepaper, for example in the deinking process or at the filler flotation stage.

The internal hydroxy mixed ethers according to the invention may be used individually. However, it can be of advantage

for the dewatering of certain solids to combine products differing in their chain length or degree of alkoxylation with one another to utilize synergisms of their physicochemical properties. Similarly, it can be of advantage to use combinations of the internal hydroxy mixed ethers with other already known ionic or nonionic dewatering aids.

In one advantageous embodiment of the process according to the invention, the internal hydroxy mixed ethers are used in quantities of 10 to 500 g, preferably in quantities of 50 to 300 g and, more preferably, in quantities of 150 to 250 g, based on the solids content, per ton solids.

The following Examples are intended to illustrate the invention without limiting it in any way.

Examples

I. Production Examples

A) Hydroxy mixed ethers based on oleic acid methyl ester epoxide.

374 g (1 mol) butyl diglycol-5EO-ether and 5 g sodium methylate (30% solution in methanol) were heated in vacuo to 60°C to remove the methanol introduced with the catalyst. After addition of 312 g (1 mol) oleic acid methyl ester epoxide (EDENOR® MeTiO$_5$ epoxide, a product of Henkel KGaA, Düsseldorf, FRG), the mixture was heated for 130 minutes to 160°C. The hydroxy mixed ether was obtained as a clear liquid in a substantially quantitative yield.

Characteristic data of the product:

Pour point	: 9 °C
Viscosity (Höppler)	: 60 mPa.s
Hydroxyl value	: 81
Saponification value	: 88
Iodine value	: 15.2
Acid value	: 1.1
Residual epoxide oxygen content	: 0.1% by weight

B) Hydroxy mixed ether based on soybean oil epoxide

As in Example A), 748 g (2 mol) butyl diglycol-5EO-ether and 5 g sodium methylate (30% solution in methanol) were heated in vacuo to 60°C to remove the methanol introduced with the catalyst. After addition of 929 g (1 mol) soybean oil epoxide (EDENOR® D81, epoxide oxygen content 6.5% by weight, a product of Henkel KGaA, Düsseldorf, FRG), the mixture was heated for 130 minutes to 160°C. The hydroxy mixed ether was obtained as a clear liquid in a

substantially quantitative yield.

Characteristic data of the product:

Pour point	: -7 °C
Residual epoxide oxygen content	: 0.1% by weight
Viscosity (Höppler)	: 33 mPa.s
Hydroxyl value	: 131

C) **Hydroxy mixed ether based on alpha-tetradecene epoxide**

As in Example A), 374 g (1 mol) butyl diglycol-5EO-ether and 5 g sodium methylate (30% solution in methanol) were heated in vacuo to 60°C to remove the methanol introduced with the catalyst. After addition of 212 g (1 mol) alpha-tetradecene epoxide, the mixture was heated for 130 minutes to 160°C. The hydroxy mixed ether was obtained as a cloudy liquid in a substantially quantitative yield.

Characteristic data of the product:

Pour point	: 13 °C
Viscosity (Höppler)	: 70 mPa.s
Hydroxyl value	: 100
Residual epoxide oxygen content	: 0.1% by weight

Products A) and B) correspond to the invention, product C) is intended for comparison.

II. Dewatering of quartz sand

Quartz sand having the following particle size distribution was used for the dewatering tests:

> 125 µm : 2.8% by weight
125 to 200 µm : 26.4% by weight
200 to 315 µm : 60.1% by weight
> 315 µm :10.7% by weight

The tests were carried out in a bucket centrifuge with which centrifugal values of 15 to 2,000 can be obtained. Perforated plates with 0.1 x 2 mm sieve openings were used for the screens. The dewatering aids were used in aqueous solutions. All concentration figures are based on solids.

After the quartz had to be weighed into the buckets of the centrifuge, the aqueous solutions of the dewatering aids were poured over the layer. After a drainage time of 1 minute, the solids were dewatered for 30 s at a rotational speed of 500 r.p.m. The moist solids were then weighed out, dried to constant weight at 100°C and the residual moisture content and reduction in the residual moisture content in %-rel were determined. All the test results are averages of double determinations. The results are set out in Table 1.

Table 1: Dewatering of quartz sand

Ex.	Aux.	Residual moisture %-rel.			Red. in residual moisture %-rel		
		E1	E2	E3	E1	E2	E3
1	A	5.7	4.4	4.4	1.9	2.6	2.7
2	B	5.8	4.8	4.8	1.8	2.3	2.3
C1	None	7.6	7.1	7.1	-	-	-
C2	C	5.4	5.0	4.5	2.2	2.1	2.6

Legend:
Aux. = Auxiliary
E1 = Quantity weighed in 150 g auxiliary/t solid
E2 = Quantity weighed in 250 g auxiliary/t solid
E3 = Quantity weighed in 350 g auxiliary/t solid

III. Dewatering of iron ore concentrate

The in-plant filter feed of an iron ore concentrate was used for the dewatering tests. the tests were carried out in a pressure filter (60 cm²); pressure difference 2 bar. The filter

feed had a solids content of 65% by weight, the sample volume was 120 ml. The dewatering aids were again used in aqueous solutions. All concentration figures are based on the solids. After dewatering, the moist solids were weighed out, dried to constant weight at 100°C and the residual moisture content determined in %-rel. All the test results are averages of double determinations. The results are set out in Table 2.

Table 2: Dewatering of iron ore concentrate

Ex.	Aux.	Residual moisture %-rel.			Red. in residual moisture %-rel		
		E4	E5	E6	E4	E5	E6
1	A	7.3	7.1	7.1	0.2	0.4	0.4
2	B	7.5	7.3	6.8	–	0.2	0.7
C1	None	7.5	7.5	7.5	–	–	–
C2	C	7.3	7.1	7.2	0.2	0.4	0.3

<u>Legend:</u>

Aux. = Auxiliary
E1 = Quantity weighed in 100 g auxiliary/t solid
E2 = Quantity weighed in 150 g auxiliary/t solid
E3 = Quantity weighed in 200 g auxiliary/t solid

CLAIMS

1. Internal hydroxy mixed ethers obtainable by subjecting epoxides of unsaturated fatty acid esters with fatty alcohol polyglycol ethers corresponding to formula (I):

$$R^1O\text{-}(CH_2\underset{\displaystyle |}{\overset{\displaystyle R^2}{C}}HO)_nH \qquad (I)$$

in which R^1 is a linear or branched, aliphatic C_{4-22} hydrocarbon radical and R^2 is hydrogen or a methyl group, to ring opening.

2. A process for the production of internal hydroxy mixed ethers, in which epoxides of unsaturated fatty acid esters with fatty alcohol polyglycol ethers corresponding to formula (I):

$$R^1O\text{-}(CH_2\underset{\displaystyle |}{\overset{\displaystyle R^2}{C}}HO)_nH \qquad (I)$$

in which R^1 is a linear or branched, aliphatic C_{4-22} hydrocarbon radical and R^2 is hydrogen or a methyl group, are subjected to ring opening.

3. A process as claimed in claim 2, characterized in that epoxides of unsaturated fatty acid lower alkyl esters corresponding to formula (II):

$$R^3CO\text{-}OR^4 \qquad (II)$$

in which R^3CO is an unsaturated acyl radical containing 16 to 22 carbon atoms and R^4 is a linear or branched alkyl radical containing 1 to 4 carbon atoms, are used.

4. A process as claimed in claim 2, characterized in that epoxides of unsaturated fatty acid glycerol esters corresponding to formula (III):

$$\begin{array}{l} CH_2O\text{-}COR^4 \\ | \\ CH\text{-}O\text{-}COR^5 \\ | \\ CH_2O\text{-}COR^6 \end{array} \qquad (III)$$

in which R^4CO, R^5CO and R^6CO independently of one another represent unsaturated acyl radicals containing 16 to 24 carbon atoms, are used.

5. A process as claimed in claim 2, characterized in that the epoxides and the fatty alcohol polyglycol ethers are used in a molar ratio of 1:0.5 to 1:1.15, based on the epoxide content.

6. A process as claimed in claim 2, characterized in that the ring opening reaction is carried out in the presence of basic catalysts.

7. A process as claimed in claim 2, characterized in that the catalysts are used in quantities of 0.1 to 5% by weight, based on the epoxide.

8. A process as claimed in claim 2, characterized in that the ring opening reaction is carried out at temperatures of 80 to 150°C.

9. The use of the internal hydroxy mixed ethers claimed in claim 1 as auxiliaries for dewatering fine-particle solids suspensions, particularly in the recycling of wastepaper.

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ABSTRACT OF THE DISCLOSURE

Internal hydroxy mixed ethers are obtained by a process in which epoxides of unsaturated fatty acid esters with fatty alcohol polyglycol ethers corresponding to formula (I):

$$R^1O-(CH_2\overset{\overset{\displaystyle R^2}{|}}{C}HO)_nH \qquad (I)$$

in which R^1 is a linear or branched, aliphatic C_{4-22} hydrocarbon radical and R^2 is hydrogen or a methyl group, are subjected to ring opening. The products are suitable as auxiliaries for dewatering solids and are distinguished by good biodegradability, low foaming and low pour points.